2005 DOE Hydrogen Program Review

Metal-doped Carbon Aerogels for Hydrogen Storage

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DOE Center of Excellence on Carbon-based H_2 Storage Materials

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Overview of Project

Timeline

- Project start: FY05
- Project end date: FY07
- Percent complete: New Start

Budget

- Total project funding (proposed): $1050K
- Funding for FY05: $240K

Technical Barriers Addressed by Project

B. Weight and Volume
C. Efficiency
M. Hydrogen Capacity and Reversibility
N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- NREL (Heben/Dillon)
  - H2 uptake/release measurements
- UNC-Chapel Hill (Prof. Wu)
  - Advanced NMR analysis
- Oak Ridge (Gregory)
  - NMR analysis of materials
- MIT (Prof. Dresselhaus)
  - Materials Characterization

Project Objectives

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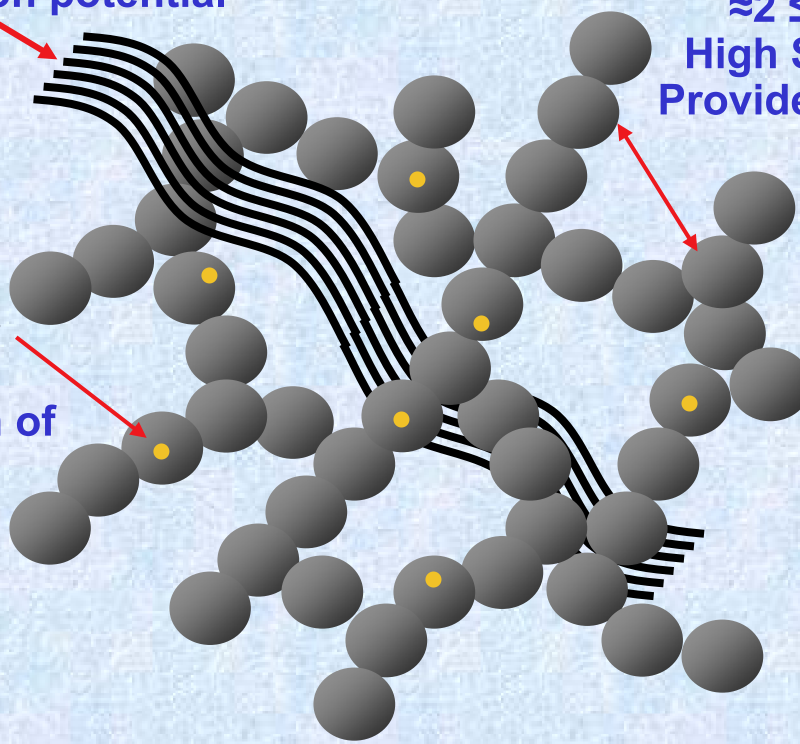
- To develop new nanostructured carbon materials that meet the targets set by DOE for hydrogen storage:
  - Novel metal-doped carbon aerogels (MDCAs) will be prepared, characterized and evaluated for their hydrogen storage properties
  - Mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques
- Insights gained from MDCA systems should also be beneficial to the other nanostructured carbon systems, leading to the design of an optimized carbon-based material for hydrogen storage

Technical Approach

- **Metal-doped CAs possess desirable structural features for the investigation of hydrogen uptake and release:**

Graphitic Nanostructures
Nanoporosity
Curved surfaces for increased adsorption potential

Mesoporosity
≈2 ≤ d ≤ ≈50 nm
High Surface Areas
Provides accessibility



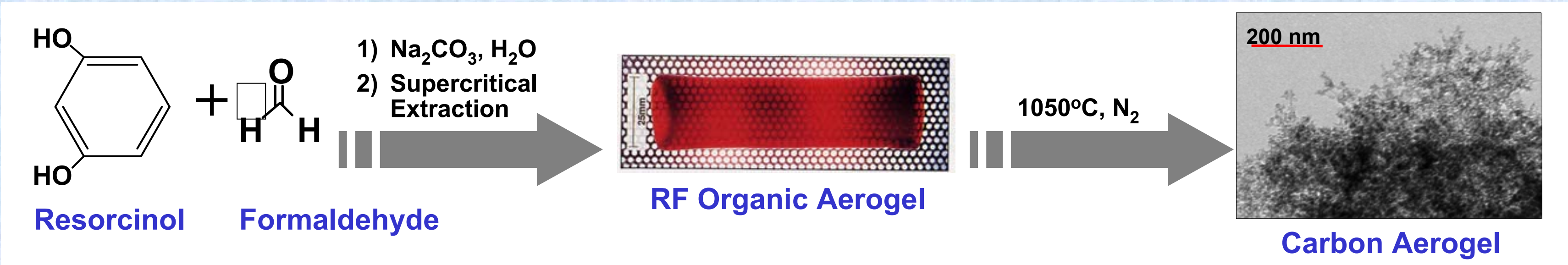
Metal Nanoparticles
d = 5 to 60 nm
Catalyze the formation of graphitic structures

Primary carbon particles
d = 2 to 20 nm
Amorphous or Graphitic?
Contain microporosity

Metal-doped CAs can be readily prepared in bulk quantities (gram scale)

Background on Carbon Aerogels

- **Novel mesoporous materials:**
  - Low mass densities (0.5-0.01 g/cm^3)
  - High surface areas (400-1000 m^2/g)
  - Ultrafine cell/pore sizes
  - Continuous porosities
- **Prepared using sol-gel chemistry:**



- **H_2 storage properties of undoped CAs have been investigated:**
- **Flexibility of organic sol-gel chemistry can be exploited to improve H_2 storage capacity in carbon aerogels**

Aerogel	Density (g/cm^3)	H_2 (wt%)	H_2 (kg/m^3)
RF	0.106	16.7	21.3*
RF	0.411	4.4	19.3
CA	0.149	5.8	9.3
CA	0.637	3.2	21.0

Measurements were performed at 77 K, *1000 psi
(Pekala et al. 1995, UCRL-JC-120315)

Current Technical Status

FY05 Accomplishments:

1. Preparation of MDCAs:

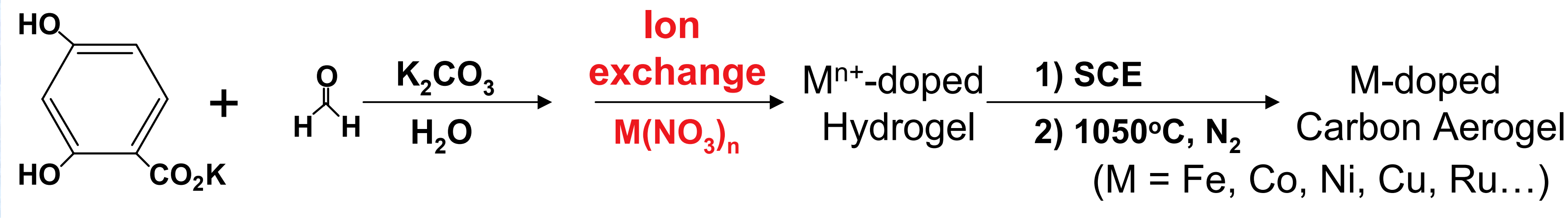
- Different metals: Co, Ni, Fe (~8-10 wt% M-loading)
- Different densities: 200 mg/cc, 400 mg/cc
- Different carbonization temperatures: 800^{o}C, 1050^{o}C

2. Structural characterization:

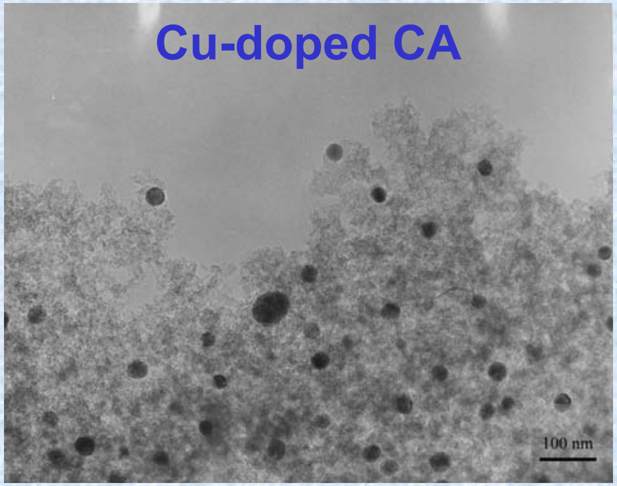
- SEM, TEM, XPS, and XRD (Collaboration with Dresselhaus Group at MIT)
- Examining carbon structure in MDCAs using solid state ^{13}C NMR techniques
- Currently using ^{129}Xe NMR experiments to probe textural porosity (LLNL/PNNL Collaboration: *J. Am. Chem. Soc.* **2004**, *126*, 5052)

Current Technical Status

- **Incorporation of metal species into aerogel framework using sol-gel precursors containing ion exchange sites :**
  - **General technique that can be used to incorporate a variety of metals**



- **Physical Properties:**
  - Density Ranges: 150-400 mg/cm^3
  - Surface Areas: 500-900 m^2/g
  - Metal Content: 1-10% by weight
- **Metal nanoparticles form during carbonization (5 to 60 nm)**



Satcher, J. H.; Baumann, T. F., *US Patent 6 613 809*, **2003**.

Baumann, T. F. et al *Langmuir*, **2002**, *18*, 7073; *Langmuir*, **2002**, *18,* 10100; *J. Non-Cryst. Solids* **2003**, *317*, 247 *J. Non-Cryst. Solids*, **2003**, *318, 223*.

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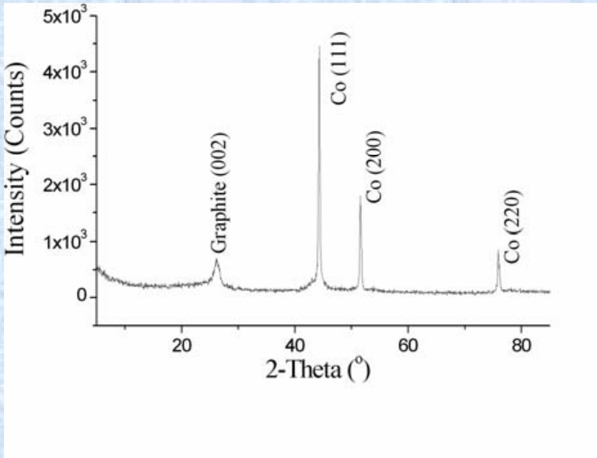
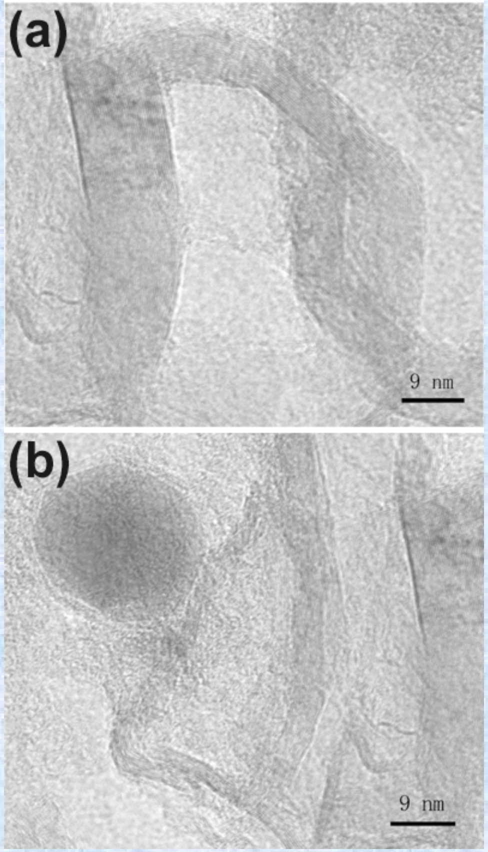
Current Technical Status

- **Formation of graphitic nanostructures in our MDCAs (M = Co, Ni, Fe) observed at relatively low carbonization temperatures**
  - **XPS data show metal nanoparticles coated with graphitic carbon**
  - **Potential substrates for the growth of carbon nanotubes**



Co-doped CA (T_c = 1050°C)

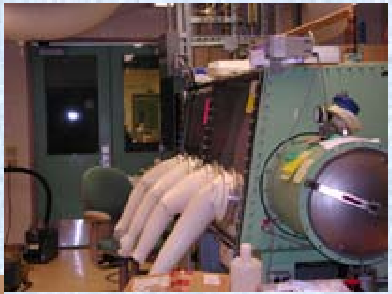


Baumann, T. F. et al *Langmuir*, **2005**, *in press*.

LLNL Sol-Gel Synthesis Facilities

- **Laboratory Space:**
  5 Labs totaling ~3000 ft^2
- **Equipment:**
  2 Rapid Super Critical Extractors
  20L High Temperature Extractor
  16L CO_2 Extractor
  10 Polaron CO_2 Extractors
  5 Lindberg Tube Furnaces
  Programmable Sintering Furnaces
  High Temp Vacuum Furnace
  Clean Room
  Quench Furnace
  Glove Box






Current Technical Status

- **Solid state NMR techniques will be used to:**
  - Determine the nature of metal-carbon, carbon-hydrogen and metal-hydrogen interactions utilizing *in-situ* ^{1}H, ^{2}H, ^{1}H-^{13}C and ^{1}H-M (where M = ^{59}Co, ^{61}Ni, ^{57}Fe, ^{11}B and ^{27}Al) NMR
  - Determine the mode of hydrogen interaction with the MDCAs
- **These experiments will allow us to assess the most favorable combinations of carbon-metal-hydrogen and relevant structural motifs for optimal hydrogen storage**
- **We are currently using NMR methods to examine the structure and dynamics of H_2 storage in alanate systems (collaboration with SNL)**

LLNL NMR Facilities

- **LLNL has state of the art NMR facilities that compliment those at UNC:**
  - **Multiple field strengths (20, 42, 82, 300, 400, 500, 600 MHz)**
  - **Full suite of solids and liquid state NMR probes**
  - **Field gradients for diffusion and imaging experiments**
  - **OP ^{129}Xe capabilities**
  - **Cryostats capable of reaching 4K and transmission line probes for observation of in-situ H_2 adsorption**
  - **Extensive experience in the characterization of disordered materials, double resonance SEDOR experiments, and dynamics**

CNSAMR

Future Work

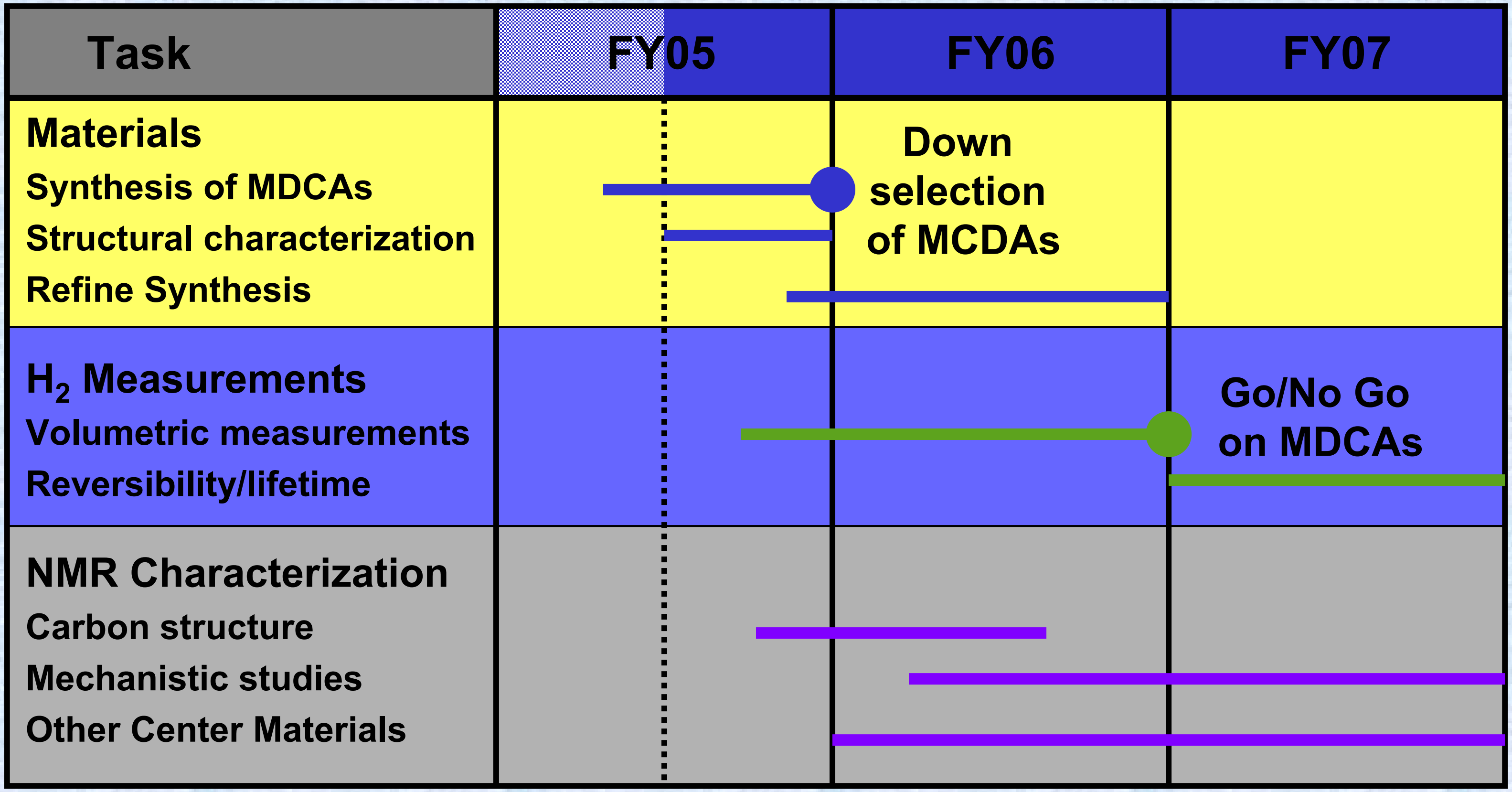
- **Evaluate H_2 storage properties for MDCAs:**
  - Currently constructing apparatus for volumetric H_2 measurements
- **Initiate mechanistic studies using advanced NMR techniques**

- **Milestones:**
  1) Down-select number of MDCAs examined
  2) Optimize H_2 storage capacities for most promising candidates through modification of:
     - Metal species (type, doping level)
     - Carbonization temperature (degree of graphitization)
     - Particle size (surface area,pore size distribution)
     - Density (weight, strength)

FY06 efforts:

- Determining reversibility and lifetime in these materials over multiple charge/discharge cycles
- Continue mechanistic studies using advanced NMR techniques

Project Timeline



Overlap with Center Members

- Interaction with National Renewable Energy Laboratory (Heben/Dillon) for H_2 adsorption/desorption measurements:
  - Measure H_2 uptake/release for the MDCA samples
  - Performed initial TPD studies on our "baseline" un-doped CA materials
- Complement NMR work at UNC-Chapel Hill (Prof. Y. Wu) in the analysis of H_2 uptake and release in carbon-based materials
  - Evaluate mechanisms of interaction using NMR techniques
  - Unique capabilities at LLNL's NMR Center
  - Discussions with groups at Oak Ridge (Dr. Gregory) and CalTech (Prof. Ahn) regarding NMR analysis of carbon-based materials
- Opportunities for developing computational effort
  - Models for growth of metal particles and graphitic nanostructures
  - Graphitic overcoat on metal nanocrystals
  - H_2 interaction with MDCAs

Hydrogen Safety for Effort

- **The most significant hydrogen hazard associated with this project:**
  - **The use of compressed hydrogen gas in the evaluation of the MDCA materials**
  - **Volumetric hydrogen measurements will require the use of hydrogen gas in a pressure manifold**
  - **The NMR experiments will involve pressurizing quartz NMR tubes with hydrogen gas**

Hydrogen Safety for Effort

- Our approach to deal with this hazard:
  - We have an integrated safety management (ISM) plan in place at LLNL for the use of hydrogen gas:
    - Personnel will have training in handling pressurized gases
    - The equipment will be tested by certified personnel to verify that all parts conform to ASME pressure standards
  - The experiments (both volumetric and NMR) will require small volumes of hydrogen gas, limiting the risk associated with this work